

[0028]

[Example]

The method for producing a ceramic powder of the present invention is described below by referring to the Example.

[0029]

First, 1.0 mol of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ as an alkoxide of Ti was dissolved in an isopropyl alcohol (hereinafter referred to as "IPA") solution to prepare a 1.0 mol/L diluted solution of alkoxide. Subsequently, this alkoxide diluted solution was divided to have a Ti amount of 0.1 mol and transferred into a beaker. To this divided alkoxide diluted solution, IPA was added to make about 200 cc and while heating at 45 to 55°C on a hot plate, 180 cc of an IPA solution containing 10% of pure water was gradually added to cause hydrolysis. After the hydrolysis, the pH was adjusted to 9 by adding aqueous ammonia. Thus, an oxide sol of Ti was produced.

[0030]

An oxide sol of Zr was produced in the same manner starting from $\text{Zr}(\text{OC}_4\text{H}_9)_4$ as an alkoxide of Zr.

[0031]

Each alkoxide diluted solution was divided to have a Ti or Zr amount of 0.05 mol and transferred to a beaker. To the resulting divided alkoxide diluted solution, IPA was added to make about 200 cc and while heating at 45 to 55°C on a hot plate, 180 cc of an IPA solution containing 10% of

pure water was gradually added to cause hydrolysis. After the hydrolysis, the pH was adjusted to 9 by adding aqueous ammonia. Thus, a composite oxide sol of Ti·Zr was produced.

[0032]

The oxide sol of tetravalent titanium group element prepared above, a hydroxide of an alkaline earth metal element and NaOH together with 500 cc of pure water and 500 cc of PSZ ball having a diameter of 2 mm were charged into a urethane-lined reactor having a content volume of 2,000 cc to have a composition ratio shown in Table 1. For stirring PSZ at a high speed, a closed cap with an impeller was set to the reactor and this reactor was fixed in an oil bath. The reaction was performed at 85°C for 3 hours while stirring PSZ at a high speed.

[0033]

After the completion of reaction, 2 mol% of Na₂CO₃ and 0.01 wt% of EDTA were added to the produced composite perovskite compound and stirred at a low speed for 30 minutes. Thereafter, the reactor was taken out from the oil bath and cooled to room temperature. Then, the reaction product was recovered and washed with pure water to remove Na⁺ and thereby obtain a composite perovskite compound powder.

[0034]

[Table 1]

Sample No.	Ba(OH) ₂ (mol)	Sr(OH) ₂ (mol)	Ti Oxide Sol (mol)	Zr Oxide Sol (mol)	NaOH (mol)
1	1.000	0	1.000	0	1.500
2	0.700	0.300	1.000	0	1.500
3	1.000	0	0.500	0.500	1.500

[0035]

The obtained composite perovskite compounds each was subjected to the analysis by X-ray diffraction (XRD), the measurement of specific surface area (SS) and the chemical analysis of molar ratio. The results obtained are shown in Table 2. The composite perovskite compound of Sample No. 2 was subjected to the molar ratio analysis at random 10 spots with a 3- μ m spot size using a transmission analysis electron microscope. The results obtained are shown in Table 3.

[0036]

[Table 2]

Sample No.	XRD Analysis Results	SS analysis Results (m ² /g)	Chemical Analysis Results of Molar Ratio Ba/(Ti+Zr)
1	Single Phase of BaTiO ₃	40	0.999
2	Single phase of (BaSr)TiO ₃	38	0.998
3	Single phase of Ba(TiZr)O ₃	41	1.001

[0037]

[Table 3]

Spot Analyzed	Analysis Results of Molar Ratio by Transmission Analysis Electron Microscope		
	Ba	Sr	Ti
1	0.700	0.299	1.001
2	0.698	0.300	0.998
3	0.706	0.294	1.000
4	0.695	0.305	1.000
5	0.700	0.297	0.997
6	0.699	0.297	1.004
7	0.694	0.305	0.999
8	0.704	0.299	1.003
9	0.694	0.301	0.995
10	0.708	0.295	1.003
Amount charged	0.700	0.300	1.000

[0038]

As seen from the results of XRD analysis in Table 2, the composite perovskite in Sample Nos. 1 to 3 obtained by the production method of the present invention were cubic crystal single phases of BaTiO_3 , $(\text{BaSr})\text{TiO}_3$ and $\text{Ba}(\text{TiZr})\text{O}_3$, respectively. Also, as seen from the results of SS measurement, the powder particles of Sample Nos. 1 to 3 each has a specific surface area of about $40 \text{ m}^2/\text{g}$ and this is as large as 10 times or more the specific surface area of conventional powder particles obtained by the calcination and pulverization of carbonate or oxide powder, revealing that the composite perovskite compound obtained by the method of the present invention is a very fine powder particle. The particle size converted from the SS value is 3 nm and almost agrees with 4 nm which is a

crystal particle size calculated from the diffraction width of XRD, and this reveals that the primary particle is equal to the crystal particle. Furthermore, as seen from the results of observation through an electron microscope, primary particles of several nm are aggregated to form a secondary particle of 0.1 to 0.3 μm . By the chemical analysis of the perovskite compound powder particles of Sample Nos. 1 to 3, the obtained compounds each is found to have a molar ratio as charged within the range of analysis error.

[0039]

Also, as shown in Table 3, the analysis result of the composite perovskite compound powder particle of Sample No. 2 at random 10 spots with a 3- μm spot size by a transmission analysis electron microscope reveals that the molar ratio is nearly the ratio as charged.

[0040]

From these results, it is verified that a composite perovskite compound powder having a composition ratio as charged, being uniformly dispersed and having a large specific ratio and high surface activity can be obtained by the production method for ceramic powder of the present invention.

[0041]

In the Examples above, an oxide sol obtained by the hydrolysis of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ or $\text{Zr}(\text{OC}_4\text{H}_9)_4$ as an organic metal compound of tetravalent titanium group element is reacted

with a hydroxide of an alkaline earth metal, however, the present invention is not limited thereto. More specifically, at least one of a hydroxide obtained by the reaction of a water-soluble inorganic compound of tetravalent titanium group element with a caustic alkali, an oxide sol obtained by the hydrolysis thereof, and an oxide sol obtained by the hydrolysis of an organic metal compound of tetravalent titanium group element, such as alkoxide, can be appropriately reacted with a hydroxide of an alkaline earth metal.

[0042]

As for the water-soluble inorganic compound of tetravalent titanium group element, chloride, oxychloride, nitrate, sulfate or the like can be used. As for the organic metal compound of tetravalent titanium group element, an alkoxide such as titanium isopropoxide, titanium butoxide, titanium ethoxide, dibutoxy-ditriethanolamine titanium, dibutoxy(2-hydroxyethyl-aminoethoxy)titanium, or other Ti organic compound can be used. As for the tetravalent titanium group elements other than Ti, the same as in the case of Ti organic compound such as Ti alkoxide can apply.

[0043]

In the Examples above, NaOH is added to form a complex $\text{Ti}(\text{OH})_6^{-2}$, however, the present invention is not limited thereto. More specifically, a caustic alkali (e.g., KOH, LiOH), NH_4OH , an aliphatic amine (e.g., methylamine,

dimethylamine, trimethylamine, ethylamine, or an aromatic amine (e.g., o-, m- or p-toluidine, N,N-dimethylbenzylamine) can be appropriately used other than NaOH.

[0044]

Furthermore, in the Examples above, Na_2CO_3 was added after the completion of reaction so as to precipitate the composite perovskite compound dissolved in a light amount, however, the present invention is not limited thereto. More specifically, a carbonate such as K_2CO_3 , Li_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ can be appropriately used other than Na_2CO_3 .

hydrolysis is accelerated, and a titanium oxide sol with a large particle size and poor dispersion properties is obtained. When the concentration is less than about 0.01 mol/L, the density of the titanium oxide particles in the obtained sol is decreased, which lowers the productivity.

A metal salt for use in the present invention which comprises at least one of Ca, Sr, Ba, Pb, or Mg is not particularly limited as long as any of the above-mentioned metals are contained. It is preferable that such a metal salt be water-soluble. Usually, a nitrate, an acetate, or a chloride salt is usable. These metal salts may be used alone, or two or more metal salts may be mixed in an arbitrary ratio. More specifically, when the metal salt contains Ba, barium chloride, barium nitrate, and barium acetate are usable; and when the metal salt contains Sr, strontium chloride, strontium nitrate, and strontium acetate are usable.

The method for producing a sol in which the perovskite titanium-containing composite oxide particles are dispersed according to the present invention comprises the step of allowing the titanium oxide particles with a brookite crystalline form, or the titanium oxide sol obtained by subjecting a ~~titanate~~ to

titanium salt ✓